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Configurational interaction studies of the lower excited states in some aromatic molecules

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Transition energy values and oscillator strengths of α- p- and β-bands of benzene, the different fluoro-substituted benzenes and pyridine molecules have been calculated by the CNDO/S method of Delbene & Jaffe' using 70 lower singly excited states for configuration interaction. Fairly good agreement between the observed and the presently computed transition energies, representing the α^- and β^- bands in benzene, pyridine and the fluoro-substituted benzenes has been obtained. However, for the p -band, though the theoretical results for benzene, pyridine and fluorobenzene are close to the experimental values, those for the remaining molecules do not show good correspondence with the observed data. The probable causes for these differences have been discussed in the present paper.

1. INTRODUCTION

As a result of extensive theoretical studies under π-electron approximation with configuration interaction (Pariser—Parr-Pople method) the characteristics of the singlet—singlet transitions in benzene and some simply substituted benzenes are now fairly well understood. However, in many polysubstituted benzene molecules the results obtained by this method have not been satisfactory and this deficiency has been variously attributed to the inadequacy of the same set of parameters for all the molecules (Rastogi & Ray 1974), the exclusion of σ-valence orbitals and non-inclusion of the doubly excited states (Delbene & Jaffe' 1968), etc. From these calculations Brown & Hefferman (1958, 1959) tried to improve the PPP method by adopting the self consistent electronegativity scheme in which some of the parameters in these calculations are adjusted through the variation of the orbital exponent of a given atom with the electron density round that particular atom. Mishra & Rai (1973) applied the method to compute the transition energies and oscillator strengths, only for the α-band system, of some of the di- and tri-homosubstituted benzene molecules. Later, Rastogi & Ray (1974) also used the same method to compute energies of the α, p and β transitions of some mono-, di- and trifluoro substituted benzenes. But the transition energies, calculated by them, for the α-band system, are much lower than those observed experimentally and similar comparisons with the other two transitions were not made by them.

Earlier, Delbene & Jaffe' (1968) introduced the CNDO/S method in which the π-electron scheme of calculation was modified by including the σ-valence orbitals. Using configuration interaction from thirty singly excited states they were able to obtain good agreement between the calculated and observed transition energies in benzene and pyridine molecules. However, such calculations with poly-substituted benzene molecules have not, to our knowledge, appeared in the literature. Recently, absorption studies in the far ultraviolet region in a large number of fluoro-substituted benzenes have been reported by Gilbert *et al* (1972). It was, therefore, thought worth while to carryout the CNDO/S calculations of Delbene and Jaffe' for these molecules to find out how far the theoretical results agree with the experimental observations. The results obtained with the moleculess of benzene, fluorobenzenes and pyridine are presented in this paper.

2. Method of Calculation and Results

Transition energy values and oscillator strengths of α, *p*- and and β-bands of benzene, the different fluoro-substituted benzenes and pyridine have been calculated by the CNDO/S method of Delbene & Jaffe' (1968) using 70 lower singly excited states for configuration interaction. Internal geometrical parameters of these molecules required for the calculation have been taken from the published literature. The computed values for the transition energies and oscillator strengths for the α, *p*- and β-bands of the above molecules are listed in tables 1-3, together with the corresponding available experimental data and theoretical results reported by other workers.

3. Discussions

Brief description of the results of the present calculations for the α-, *p*- and β-bands of the various benzenoid molecules are given separately in the following paragraphs. Some features of the method employed are also discussed.

α-band :

Results presented in table 1 show good agreement between the observed and the calculated excitation energies for this band system in benzene, mono-, di- and tri-fluorobenzenes and in pyridine but such comparison in the cases of tetra-, penta- and hexafluorobenzenes could not be made for want of experimental data. It is also seen from table 1 that the values of the transition energies calculated by Rastogi & Ray (1974) using variable electronegativity scheme are considerably lower than those of present investigation. However, according to both the methods the transition energy decreases systematically with increase in the number of fluorine atoms in the phenyl ring. This trend is also apparent from the experimental data but the variation is not systematic. The calculated

oscillator strengths are of qualitative interest only in so far as these point to the forbidden character of the transition even in the substituted benzenes having symmetry lower than that of benzene.

Table 1. Energy and oscillator strength of α band of benzene, fluoro-benzenes and pyridine

Molecule	Transition energy in ev. Calc. Ours.	Calc. Others[b]	Expt.	Oscillator strength Calc. Ours.	Calc. Others	Expt.
B	4.84	4.70[a]	4.88[c]	0.000	0.000[a]	
FB	4.82	4.57	4.75[c]	0.001		0.029[c]
(1,2)	4.74	4.55		0.001		
(1,3)	4.74	4.55	4.70[d]	0.002		0.008[d]
(1,4)	4.74	4.54	4.57[d]	0.003		0.021[d]
(1.2,3)	4.66			0.000		
(1,2,4)	4.66	4.53	4.60[d]	0.002		
(1,3,5)	4.67	4.52	4.77[d]	0.000		
(1,2,3,4)	4.58			0.000		
(1,2,3,5)	4.59			0.001		
(5)	4.51			0.001		
(6)	4.43			0.000		
Py	4.91	4.80[a]	4.80[e]	0.066	0.017[a]	0.030[e]

*In this and in the other two tables the following abbreviations have been used : B, benzene Py, Pyridine FB. fluorobenzene (1,2). 1,2-difluoro-benzese and so on.

(a) Delbene & Jaffe' (1968).

(b) Rastogi & Ray (1974) ; unless otherwise mentioned

(c) DMS UV atlas of organic compounds (1968)

(d) Petruska (1961).

(e) Perkin & Innes (1965).

p-band :

A scrutiny of the calculated transition enerfies for this band system in the different molecules presented in table 2, reveals that the theoretical values in all the molecules except benzene, fluorobenzene and pyridine

are much lower than those obtained experimentally. Such discrepancy even in the case of benzene and pyridine molecules was noted by Delbene & Jaffe' (1968) who used 30 configurations in their C.I. calculations. The present study with 70 lower singly excited states shows considerable improvement in these two cases. Further, from a comparison with the results of Rastogi & Ray (1974), it is found that except for fluorobenzene, the present calculated values of the other poly-fluorobenzenes are not much different from those reported by them. Moreover, in this case also the calculated transition energy decreases with increase in the number of fluorine substitutions. This is contrary to the experimental observations.

Table 2. Energy and oscillator strength of *p*-band of benzene, fluorobenzenes and pyridine

Molecule*	Transition energy in ev			Oscillator strength		
	Calc.		Expt.*	Calc.		Expt.*
	Ours.	Others[a]		Ours	Others.	
B	6.10	5.20[b]	6.21	0.000	0.000[b]	
FB	6.02	5.86	6.24	0.034		
(1,2)	5.90	5.82	6.21	0.050		
(1,3)	5.91	5.82	6.23	0.039		
(1,4)	5.87	5.82	6.24	0.136		
(1,2,3)	5.82			0.002		
1,2,4)	5.75	5.79	6.22	0.139		
(1,3,5)	5.83	5.79	6.21	0.000		
(1,2,3,4)	5.70		6.44	0.035		
(1,2,3,5)	5.70		6.19 6.52	0.043		
(5)	5.60		6.36	0.042		
(6)	5.52		6.38	0.000		
Py	6.12	5.4[b]	6.2	0.088	0.002[b]	0.200

The average oscillator strength for benzene and different fluorobenzenes is 1.1000.

*Experimental data for the benzenes are from Gilbert *et al* (1972) (transition energies given in cm^{-1} have been converted into ev.) and those for pyridine are from Perkin and Innes (1965).

(a) Rastogi & Ray (1974) : unless otherwise mentioned.

(b) Delbene & Jaffe' (1968).

The computed oscillator strengths in all the cases except benzene, 1, 3, 5-trifluoro and the hexafluorobenzene are different from zero though the values are mostly smaller than those determined from experimental measurements (table 2). The theoretical f-value in benzene, 1, 3, 5-trifluoro and the hexafluorobenzene indicates that the transition corresponding to the p-band in these molecules is forbidden while in the remaining molecules this band should appear with intensities greater than those for the α-band in the same molecules (table 1).

β-band:

The E_{1u} excited state of benzene splits into two levels in substituted benzenes of lower symmetry and generally, two transitions, corresponding to the β-band, should occur. The two values of the transition energy computed for benzene and hexafluorobenzene molecules in the present study (table 3) are due to the assumption of D_{2h} symmetry for the respective molecules, but in the remaining substituted benzenes, excepting 1, 3, 5-trifluorobenzene, the two calculated values correspond to the two split components. The two components in 1, 3, 5-trifluorobenzene arise from the assumed C_{2v} symmetry instead of the usual D_{3h} symmetry for the molecule. However, experimentally only one band system has been observed in all the molecules by Gilbert *et al* (1972) and, therefore, it is not possible to correlate exactly the positions of the observed bands with the calculated transition energy values. Nonetheless, it is seen from table 3 that the agreement between the observed and the higher component of the calculated energy values is fairly good, the difference being <0.3 ev. in most cases. On the other hand, though the results obtained by Rastogi & Ray (1974) in some of the molecules seem to be in better agreement with the corresponding experimental values, these are not significant because their calculations do not reveal the expected splitting of the band. It is further noted that as the number of fluorine atoms in the phenyl ring is increased the calculated energy values of this transition decrease which is also observed from the experimental data. It is also gratifying to find that for these transitions, particularly in the case of the higher energy component, the computed oscillator strengths of benzene, pyridine and of all the fluoro-substituted benzene molecules are in satisfactoric agreement with the corresponding observed results.

4. Conclusion

From the features of the calculations reported in the above paragraph certain characteristics of the CNDO/S method of calculation may be discerned. The computed transition energies corresponding to the α-band in most of the molecules are within 0.1 ev. of the corresponding experimental values. An earlier computation with benzene molecule using 60 excited configurations yielded results scarcely different from those obtained in the present investigation. This

Table 3. Energy and oscillator strength of β-band of benzene, fluoro-benzenes and pyridine

Molecule	Transition energy in ev. Calc. Ours.	Calc. Others[a]	Expt.*	Oscillator strength Calc. Ours.	Calc. Others.	Expt.*
	6.77			1.060		
B		6.90[b]	7.07		0.593[b]	
	6.81			1.050		
	6.59			0.991		
FB		6 88	6.88			
	6.72			1.088		
	6.52			0.936		
(1,2)		6.65	6.76			
	6.60			1.099		
	6.39			0.875		
(1,3)		6.65	6.76			
	6.46			1.030		
	6.34			0.873		
(1,4)		6.66	6.81			
	6.57			0.927		
	6.30			0.944		
(1,2,3)						
	6.36			0.953		
	6.31			0.784		
(1,2,4)		6.62	6.68			
	6.42			0.989		
	6.36			0.972		
(1,3,5)		6.62	6.73			
	6.36			0.973		
	6.22			0.895		
(1,2,3,4)			6.48			
	6.24			0.948		
	6.19			0.912		
(1,2,3,5)			6.56			
	6.29			0.944		
	6.11			0.542		
(5)			6.41			
	6.14			0.975		
	5.99			0.923		
(6)			6.39			
	5.99			0.923		
	6.84			0.842		
Py		7.1[b]	7.00		0.473[b]	1.300
	6.97			0.893		

The average oscillator strength for benzene and different fluorobenzenes is 1.100.

*Experimental data for the benzenes are from Gilbert *et al* (1972) (transition energies given in cm^{-1} have been converted into ev.) and those for pyridine are from Perkin & Innes (1965).

(a) Rastogi & Ray (1974); unless otherwise mentioned.

(b) Delbene & Jaffe' (1968).

shows that at least for this lowest transition the limiting accuracy of the method has been reached. Moreover, the good agreement obtained also for the other molecules indicates that the parameters used are reasonable and require little change. For the β-band the calculated results may be considered fairly satisfactory though the possibility of some further improvement from the use of larger number of configurations cannot be entirely ruled out.

The greatest discrepancy is found in the case of *p*-band and the difference between the calculated and observed value increases steadily from about 0.3 ev. in the difluorobenzenes to about 0.9 ev. in hexafluorobenzene molecule. According to Delbene and Jaffe' (1968) this discrepancy may partly be due to the neglect of the three and four center integrals and partly to the non-inclusion of doubly excited configurations in the C.I. calculation. But, as earlier noted, the present calculation with 70 excited states in benzene and pyridine substantially improved the deficiency in the results of the 30 C.I. calculations for the same molecules reported by the two authors. Thus, it may reasonably be concluded that at least in these two simple molecules the three and four center integrals and the doubly excited states may not be very important. This should also apply broadly in the other fluoro-substituted benzene molecules. That this is partially correct is also apparent from the fairly satisfactory results obtained for the β-band even in the poly fluorobenzenes. It is suggested that the difficiency in the computed results mostly arises from the non-inclusion of some important excited state configurations in the C.I. calculation and that a more extended computation would lead to fairer agreement between the observed and the theoretical results. Further work in this direction is being undertaken and the results will be communicated in due time.

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